1.0

1.1

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2.8 2.5
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3.6
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1.8

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Hydrogen Response of Palladium Coated Suspended
Gate Field Effect Transistor

By

Stanley Pons, J. Cassidy, J. Janata

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A suspended metal gate field effect transistor was studied as a hydrogen sensor and the surface processes at an electrochemically deposited Pd layer on the gate were examined.

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HYDROGEN RESPONSE OF PALLADIUM COATED SUSPENDED GATE

FIELD EFFECT TRANSISTOR.

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BRIEF

Suspended gate field effect transistor with electrodeposited palladium responds reversibly to hydrogen in the range of 3 ppm to 10^5 ppm. The mechanism of this response includes both the surface and the bulk effect of hydrogen on the electron work function of palladium.

Abstract

A suspended metal gate field effect transistor was studied as a hydrogen sensor and the surface processes at an electrochemically deposited Pd layer on the gate were examined. It has been found that the time constant as well as the magnitude of the response depends on the operating conditions particularly on the presence of oxygen. If the device is tested in air the dynamic range spans logarithmically five decades of partial pressure of hydrogen.

Introduction.

Since the first report of palladium metal oxide field effect transistor (PdMOSFET) for use as hydrogen sensors appeared in 1975,[1] there has been a growing interest in the analytical use of the palladium hydrogen system. The resulting sensors have taken the form of transistors [1], Schottky diodes, [2,3] and capacitors[4]. Although most of those sensors respond to hydrogen, some have been modified to detect other electrically neutral compounds. This is the focus of the more recent research, which should ultimately lead to multicompound sensors. Such devices have already been developed for ionic species and the methods of data acquisition and interpretation have been described [5]. A complete review of the operation of chemically sensitive field effect transistors has been published recently[6]. The properties and description of Pd MOS structures have been reviewed[7-9] as well as the fundamental properties of the palladium hydrogen system [10-15].

Suspended gate field effect transistor (SGFET) is a generic structure which can be made chemically selective for different compounds by deposition of different layers on the suspended metal gate. This has been

already demonstrated by electrochemically coating the suspended gate

with polypyrrole for use as an alcohol sensor [16,17]. The source of the

signal in Pd MOSFET has been the subject of much interest [7,8]. According

to the present model, the hydrogen is adsorbed on the palladium surface

(following a Langmuir isotherm at higher concentrations) where it

dissociates and diffuses through the bulk palladium to the Pd/SiO_2

interface. The resulting layer of hydrogen dipoles induces a potential drop

at this interface. Studies of changes of Pd work function and of the Pd

surface potential [8] have shown that this process is dominated by the

changes of the dipole potential at the Pd/insulator interface[18,19].

The exact mechanism of surface interaction between hydrogen and

palladium is still under investigation, primarily by UHV techniques . A

general outline of this mechanism is as follows: In inert atmosphere the

hydrogen can adsorb in two forms. The first is a strongly bound form [14] (r

type adsorption) present at low coverages or at low temperatures. The H

atom is situated directly above the Pd atom at the surface. The second is

a weakly chemisorbed form (s type adsorption) where the hydrogen is

situated in between the Pd atoms in the surface. The latter form which

occurs at high surface coverage is in rapid equilibrium with the bulk hydrogen and can be easily removed under vacuum . The r type adsorbed hydrogen, on the other hand, cannot be removed under vacuum at room temperature [20]. At room temperature the saturation of the metal occurs at a hydrogen to palladium ratio of 0.6 . At this point the d bands of the metal are filled and the protons are completely dissolved in the metal. Thus, the paramagnetic susceptibility has been found to be zero [10]. In this situation the Fermi level of the metal is shifted to higher energies and the surface potential increases [21]. Since the hydrogen is dissolved in the metal, the lattice is strained. The resulting change in dimensions has been used as a means for sensing hydrogen[22] and has also been examined by X-ray studies[23].

Some physical properties of the Pd MOSFET have yet to be fully explained, however, the detection of less than 10 ppm of hydrogen is routinely possible[24-26] in relatively short times.

For the detection of hydrogen at a Pd MOSFET whose surface has been oxidized the hydrogen does not reach the bulk until the surface palladium oxide has been reduced to the metal [18]. Hydrogen-containing neutral

molecules such as H_2S [27,28], NH_3 [29] and hydrocarbons[30] can be detected at palladium surfaces if the sensitivity is enhanced by thin coatings of other metals such as Ir and Rh.

The design of the present device [31] may be viewed as a logical progression from the Pd MOSFET discussed above, although its mode of operation is substantially different. It is an advance over the porous Pd gate [8,32], the cantilevered gate [33], and the Pd MOSFET with deliberately etched holes [34-36]. Conducting polymers such as polypyrrole, which has been found to be sensitive to NH_3 [37], have been electrochemically deposited on the suspended gate[16,17].

The composition of the solid insulator is quite important; The layer of SiO_2 cannot be contaminated since it is protected by a layer of inert Si_3N_4 which has been shown to be impervious to hydrogen[38]. Thus, the hydrogen spillover[39,40] leading to so called "hydrogen induced drift" is not expected to occur in devices covered with silicon nitride.

EXPERIMENTAL

The preparation of the basic device has been detailed in a previous publication[31]. The distance from the mesh to the substrate is on the order of 1000 Å. The substrate insulator is composed of a layer of Si_3N_4 (800 Å) on top of a layer of SiO_2 (800 Å). After the devices were scribed they were bonded to a TO-4 header by heating to ~400°C at which temperature a Si/Au eutectic is formed, providing excellent electrical contact. The devices were then wirebonded using an ultrasonic wirebonder (Tempress Model C series 1713) and finally encapsulated with epoxy to protect the aluminium wires. For low temperatures, Epon 825 (E.V.Roberts, 8500 Steller Dr., Culver city, CA 90230) and Jeffamine D-230 (Texaco P.O.Box 430, Bellaire, TX 77401) were used and at high temperatures Epotek H77 (Epoxytek Inc.,14 Fortune Dr., P.O Box 567, Billarica, MA 01821) was used. In each case fumed silica (Cab-o-sil,Cabot Corp., Tuscola, IL 61953) was used as a thixotropic agent. After encapsulation, the Pt mesh was connected as a working electrode in a two electrode system with Pt wire as the counter electrode. The deposition was done from the solution of

0.3M $PdCl_2$ in 0.5 M NH_4Cl acidified to pH 1 with HCl [41-43]. A series of current pulses (i = 800 $\mu A/cm^2$, pulse width 10 ms) was applied to the mesh in order to deposit a total of 0.8 micromoles of Pd corresponding to an average thickness of 100 Å. It was found that at low current densities (20 $\mu A/cm^2$), the deposited metal consisted of grains of amorphous Pd black . At higher current densities (>900 $\mu A/cm^2$) a shiny deposit was obtained. An inherent disadvantage of this method of deposition is the lack of control of the potential at the working electrode. Concomitant evolution of hydrogen which could cause a phase transition could therefore not be excluded.

The testing system consisted of a Carle Gas Chromatograph (model 211 c) which was adapted to accomodate a FET transistor as described previously [17]. A separate heating tape was used to control the temperature of the FET detector block. The transistor current was controlled by means of a feedback circuit [6,44]. Gases were used as received from Liquid Air Corporation (Geneva Rd.,Orem, Utah) and were calibrated against standards (Ideal Gases Ltd. 977, New Durham Rd., P.O.Box 807, Edison , NJ 08878). Deposition of Pb was carried out from a

fluoroborate bath [41] and Zn was deposited from a cyanide bath [45]. The effect of the deposition of these metals on the H_2 response was examined.

RESULTS AND DISCUSSION

Figure 1 shows a plot of the source to drain current I_d against gate voltage V_g. The drain to source voltage V_d was 1 V and the scan rate was 100 mV/sec. The V_g/I_d curve was recorded on a Hewlett Packard semiconductor parameter analyzer (model 4145 A) interfaced to a HP 9872C plotter. The SGFET (curve2) and the Pd SGFET (curve 3) are compared to the response of a MOSFET on a similar chip . As expected for the SGFET the current is lower. The equation for the characteristic curve for a MOSFET operated in saturation is

$$I_d = \frac{n_e\, C_0'\, W}{2L} (V_g - V_T)^2 \qquad (1)$$

where V_T is the threshold voltage , C_0' is the gate capacitance. W and L

are the gate width and length respectively, and n_e is the electron mobility . This equation applies to the SGFET when an air-gap capacitance C_G is placed in series with the solid insulator gate capacitance C_0 yielding overall capacitance :

$$C_0{}' = C_G C_0/(C_G+C_0) \qquad (2)$$

Because C_G is a reciprocal function of the thickness of the air gap it follows that as the thickness decreases, the capacitance and the current increases . The threshold voltage becomes more negative since it is related to C_0 and to the work function difference between the deposited metal and the semiconductor. The downward bending of the experimental I_d - V_g curves seen in Fig.1 is due to the presence of series resistance in the N-diffusions in the transistor chip [46].

The kinetic experiments consisted of examining the response for concentration steps from a background to a certain concentration of H_2. Both the rising and falling transients were studied (Figure 2). The

response of the thermal conductivity detector (T.C.D.) in parallel with the FET detector showed that the concentration step itself had a very short rise time and that the slow rise time in the case of the FET was due to the slow kinetics at the surface. In Figure 3 a function related to a first order process ln(A/x), where A and x are defined in Figure 2, is plotted against time as a function of temperature. The first order process is dominant only for low concentrations on the rising part of the transient. The slope is seen to increase with temperature and a rate equation of the following general type can be formulated for the slowest step of the process[11]:

$$\text{rate} = (1-\Theta)^2 K_1 \exp(-2E_1/RT) \qquad (3)$$

where Θ is the fraction of occupied sites, which in the case of small concentrations is small enough for the first term in Eq.(3) to be ignored. E_1 represents the activation energy for chemisorption [11] and is shown in Figure 4. In this Figure the potential energy of the s type adsorbed hydrogen atom is shown for the most stable position is 0.5 Å below the surface of the metal [14]. The constant K_1 is the flux of the species to the surface and includes a term for the sticking coefficient .

If the s type hydrogen is present there is an immediate rapid equilibrium formed with the bulk of the metal and the alpha hydride is formed . According to some authors the signal is derived from this phase transition[4]. A first approximation proposed by Lundstrom[47] which is based on the relationship between the gate potential and the dipole moment created by the adsorbed hydrogen does not correlate well with the response of our devices.

The effect of the ratio of bulk to surface states has been observed by thermal desorption studies of palladium powder, foil and wire . In the case of the wire the diffusion from the bulk is limiting but the model is complex due to a moving phase boundary and no simple solution has been found [48].

At higher concentrations, on the rising transient, the situation is more complicated (Figure 5). For a set of temperatures, at longer times, the curves tend toward a constant slope independent of temperature. The deviation at short times might be due to the change in the type of hydrogen occupied sites θ. At longer times the process is limited by diffusion from the surface into the bulk where the rate for this process is given by

$$rate = \Theta \, K_2 \exp(-E_2/RT) \qquad\qquad (5)$$

where $\Theta \approx 1$ and E_2 is the activation energy for the transport of hydrogen from the surface into the bulk . For the s type adsorbed hydrogen this is a relatively small barrier. The rising transient due to the exposure to hydrogen may therefore be characterized by two limiting processes. In Figure 6 the log of the rate constant as determined from the slopes of the graphs in Figure 3, is plotted against inverse temperature . This slope yields an estimate for the value of E_1 (-5.7 Kcal/mole) which compares well with that of Auer and Grabke [49] (-6.8 Kcal/mole) . Their resistance measurements were made under conditions of reduced pressure and with metal foil whereas these particular measurements were made at a Pt mesh electrochemically coated with a thin (on the order of 50-100 Å) layer of Pd.

The case of the falling transient (step-down in concentration) is depicted in Figure 7 where the term $\ln(A/x)$ related to a first order process is again plotted against time. At short times a straight line

behavior is observed indicating that when $\Theta \approx 1$ the following rate law holds :

$$rate = \Theta^2 K_3 \exp(-2 E_3/RT) \qquad (6)$$

where the hydrogen is leaving as H_2 and the barrier for removal at the surface is E_3. At short times the surface is saturated and the hydrogen leaves with an apparent first order rate. At longer times, however, the desorption is determined by a combination of the above process and the diffusion from the bulk :

$$rate = (1-\Theta)X K_4 \exp(-E_4/RT) \qquad (7)$$

where X is the atomic fraction of the atoms in the bulk and E_4 is the energy required to reach the surface from the bulk. The hydrogen desorption is very sensitive to pressure changes and an increase in pressure slows down the desorption drastically. It can be seen from Figures 5 and 7, at long times, that the lines whose slopes are independent

of temperature indicate that the process dictating diffusion into the bulk is qualitatively similar to that governing diffusion from the bulk. Because of the relative uncertainty of measuring the response at long times, no quantitative data can be obtained under these conditions.

The overall response of our transistor takes the form of a negative shift in V_T which has also been seen by Lundstrom [7]. The source of the signal, in our case, is the lowering of the electron work function of palladium. As long as the contact Pd/Pt is ohmic there should be no contribution from the possible change of the work function of the platinum layer [17]. The basic requirement for analytical use of these devices involves the characterization and regeneration of the original surface. The exposure to hydrogen is seen to be more "reversible" [26] in a carrier gas containing oxygen, than in an inert gas. However, on exposure to oxygen over long times at high temperatures the sensing surface is oxidized. There have been few explicit results in the literature about the response time for the hydrogen palladium systems. LeRoy [9] reports a rise and fall time of approximately 5 minutes for 50 ppm hydrogen in air at 150^0C and a response of 100 mV. The speed and magnitude of the response of the

sensor described herein is faster and higher, as expected, because of the ease of entry of the sample into the sensor. However, the same problems of irreversible penetration of hydrogen into the metal on first exposure in an inert gas are experienced as described by others [7].

A typical response for exposure to 100 ppm H_2 is shown in Figure 8 for two carrier gases : nitrogen and air. It is seen that the response in air is different both with respect to magnitude and characteristic shape from that in nitrogen. It appears that oxygen is irreversibly bound to the surface of the palladium even in the presence of hydrogen . Switching the carrier from nitrogen to air returns the response to the original baseline. The presence of oxygen in this case appears to clean up the surface and strip off any residual hydrogen. Thus the order of exposure of the device to oxygen and hydrogen is important; if the oxygen reaches the surface first it sticks even in the presence of hydrogen . If, on the other hand, the surface is first covered with hydrogen, then the oxygen appears to strip it off. There is no response on switching from nitrogen to air, a result which is contrary to that previously reported for Pd MOSFET[1].

The optimum operating temperature for the Pd SGFET with respect to

the time response was determined to be 140^0C. When air is used as a carrier the rising part of the transient is much slower. The sensor was stable at 100^0C under a flow of air for 24 hours and after a regeneration with 100 ppm of H_2 the same response was obtained as before (the regeneration took the form of a more slowly rising transient). The change of the threshold voltage ΔV_T as a function of hydrogen concentration in air and in nitrogen is shown in Fig. 9. The slope of the response in nitrogen between 100 ppm and 10^5 ppm is reproducible and linear (80 ± 9 mV, at 140^0 C). On the other hand the response in air is lower but uniform over the whole range from 0 to 10^5 ppm. The slope is strongly affected by the state of the platinum surface before the deposition and by the palladium electrodeposition conditions. These effects require further study.

Preliminary investigation of the deposition of other metals has been carried out. The response to the step-change of hydrogen concentration in nitrogen from 0 to 100 ppm, for layers of Pb, Zn, and bare Pt were 20,50, and 190 mV as compared to 800 mV for Pd. Because hydrogen has a very high overpotential on Pb it is not expected that this metal would produce a

hydrogen response. It is possible that the small signal obtained with Pb coated SGFET could be due to adsorption of hydrogen at the silicon oxynitride surface of the gate gap. These effects also require further study.

CONCLUSIONS

Although the Pd MOSFET is the closest relative of the Pd SGFET the fundamental difference between the operation of these two types of devices has its origin in their different structure. In the former, hydrogen enters the device through the outside Pd surface, diffuses through the bulk and creates the dipole at the SiO_2/Pd interface. It is this dipole which, according to the present theory [8], dominates the signal. On the other hand in the SGFET the gas enters the gate gap and interacts with the inside Pd surface and then diffuses into the bulk. In this case the surface rather than interface potential is involved in the response [50]. Because the response extends over a wide range of concentrations (10 - 100,000 ppm) it is probable the the bulk of Pd is also involved. This could happen either through the direct modulation of the bulk term of the work function

(at high concentrations) or through the bulk effect on the surface equilibria. Further study is required to elucidate this point.

Because all processes involved in the response are consecutive and have different time constants the time response of the signal cannot be modeled by a single time exponential (Figures 5,7,8). Furthermore, the presence of oxygen seems to affect profoundly both the the time constant and the absolute magnitude of the signal (Fig. 9). In nitrogen at low concentrations (< 10 ppm) both the rise and the recovery are slow but the magnitude of the response is very high. The preliminary data show that in air the signal is logarithmic over the whole range but the slope is strongly dependent on the palladium deposition conditions.

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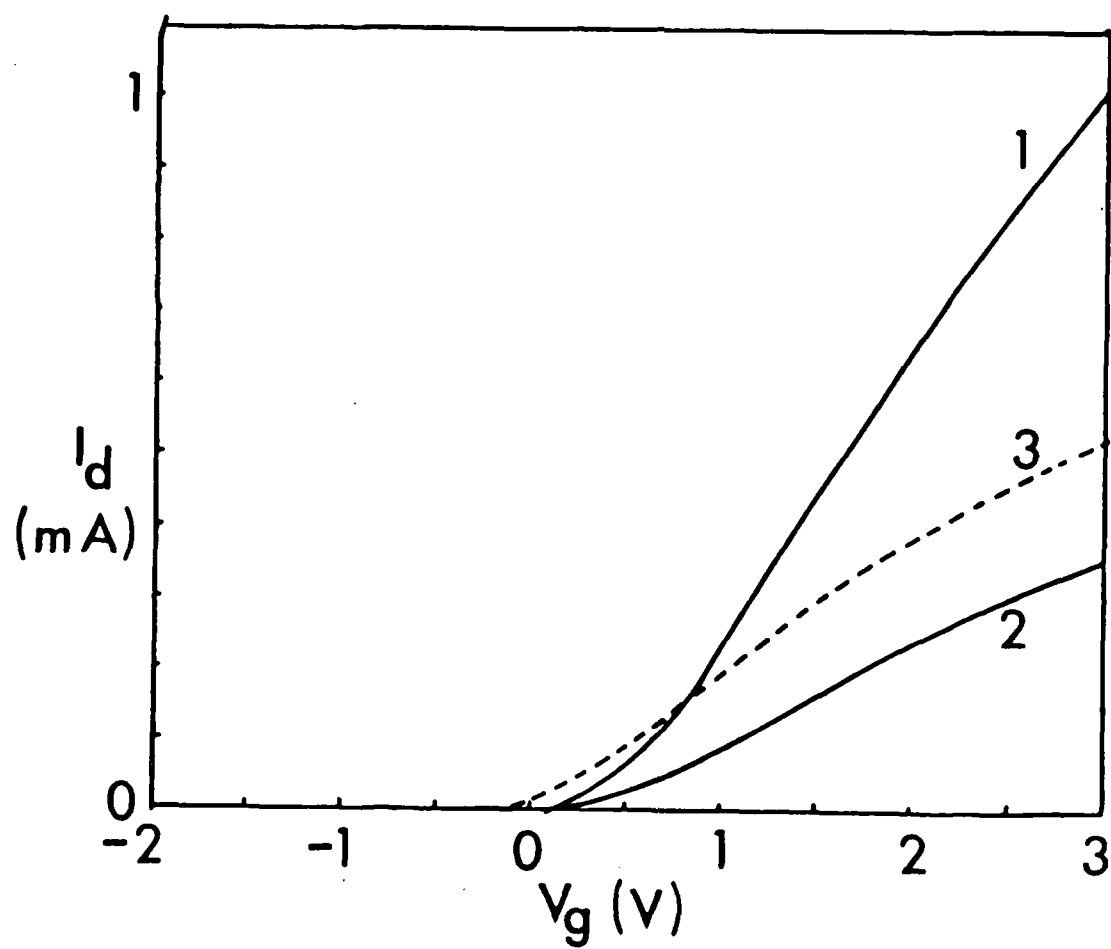50. Lundstrom,I., Sodeberg,D. Appl.Surf.Sci. 1982, $\underline{10}$, 506

Fig. 1

FIGURE LEGENDS

Figure 1. I_{DS} - V_G curves for 1: MOSFET , 2: Pt SGFET ,3: Pd SGFET,

(60 μC) . In all cases the V_D was 1V.

Figure 2. Concentration step of 1% H_2/N_2 injected into a background of

air, T=112°C. Flow rate is 30 mL/min

Figure 3 . Representation of the results in terms of a first order

parameter "ln (A/x)" . Step change from 0 to 3ppm of H_2. The

flow rate was 30 mL/min, the increasing slopes correspond to

temperatures (■) 110°,(□) 128°,(◆) 135°, and (◇) 140°C,

respectively .

Figure 4. Schematic representation of the potential energy of a hydrogen

atom in contact with palladium. E_1 is the energy of

chemisorption , E_3 is the energy required for two H atoms to

associate and leave the surface, E_5 is the energy required for

the H to get into the bulk and E_4 is the energy to leave the bulk.

Figure 5. First order kinetics representation of a rising transient for

exposure to 10% H_2 in N_2. The temperatures are (from top to

bottom) : (◇) 110°,(◆) 90°, (■) 70°,(▢) 40°,and (▲) 30° C.

Figure 6. Arrhenius plot of the rate constants found from the slopes of

the curves in Figure 3, against inverse temperature .The

concentration is 3 ppm and the rate constants are in sec^{-1} and

the temperature in °K.

Figure 7. First order representation of a falling transient for 1% H_2/N_2

concentration step. The increasing slopes are for temperatures

of (■) 90°,(◆) 100°, and (◇) 120° C, respectively.The three

regions in the figure are discussed in the text.

Figure 8. A typical response for step change from 0 to 100 ppm hydrogen

in nitrogen and air. The arrows indicate the sample injections

Increasing time is from left to right.

Figure 9. A typical plot of the change of threshold voltage ΔV_T against

hydrogen concentration in air and in nitrogen. The operating

temperature was $140^{\circ}C$.
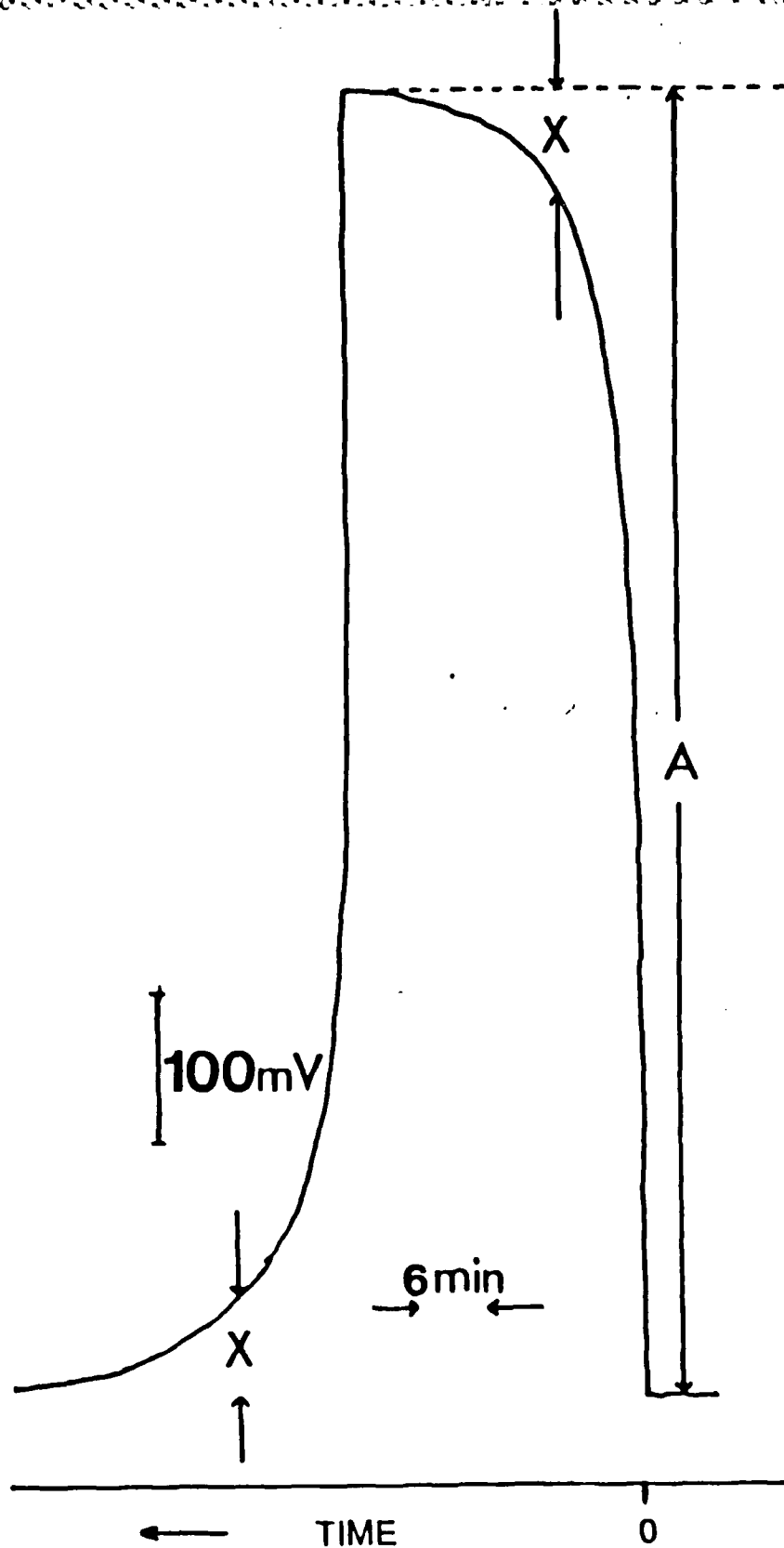
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100mV

6min

X

A

X

TIME   0

Fig. 2

Fig. 3

METAL   GAS
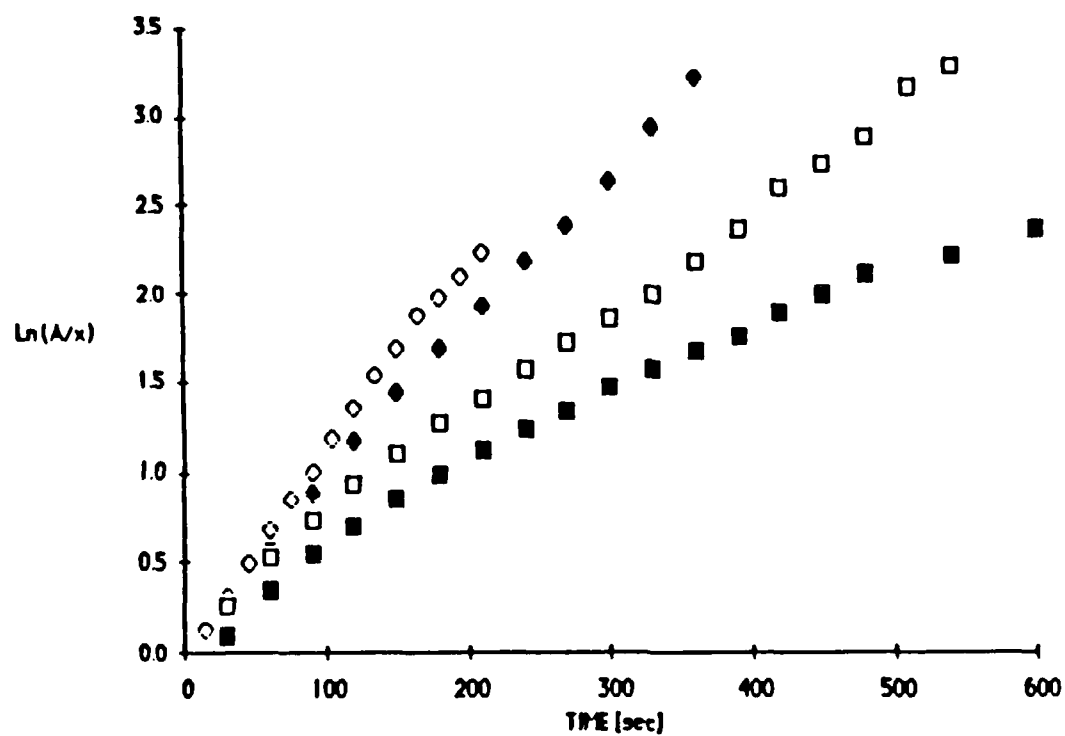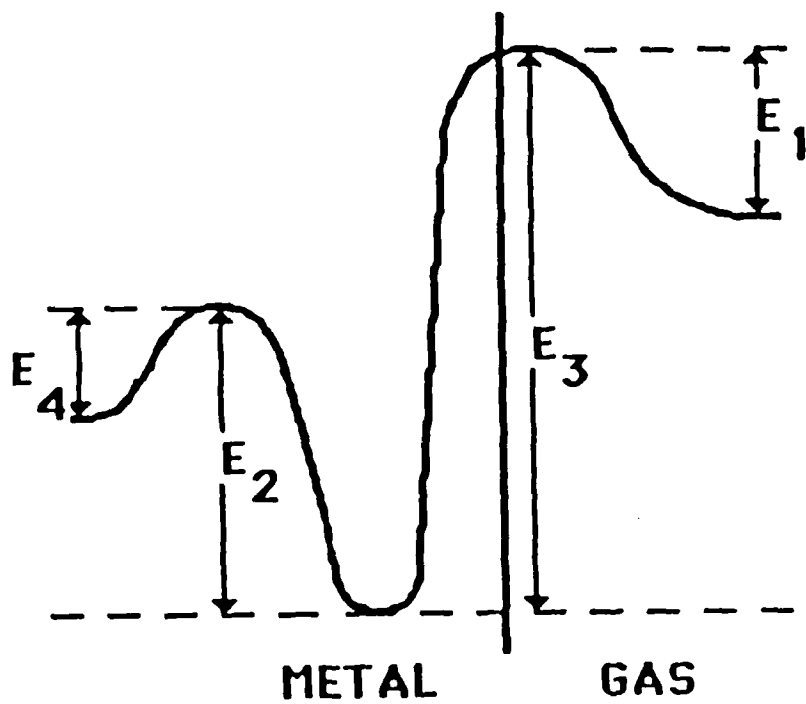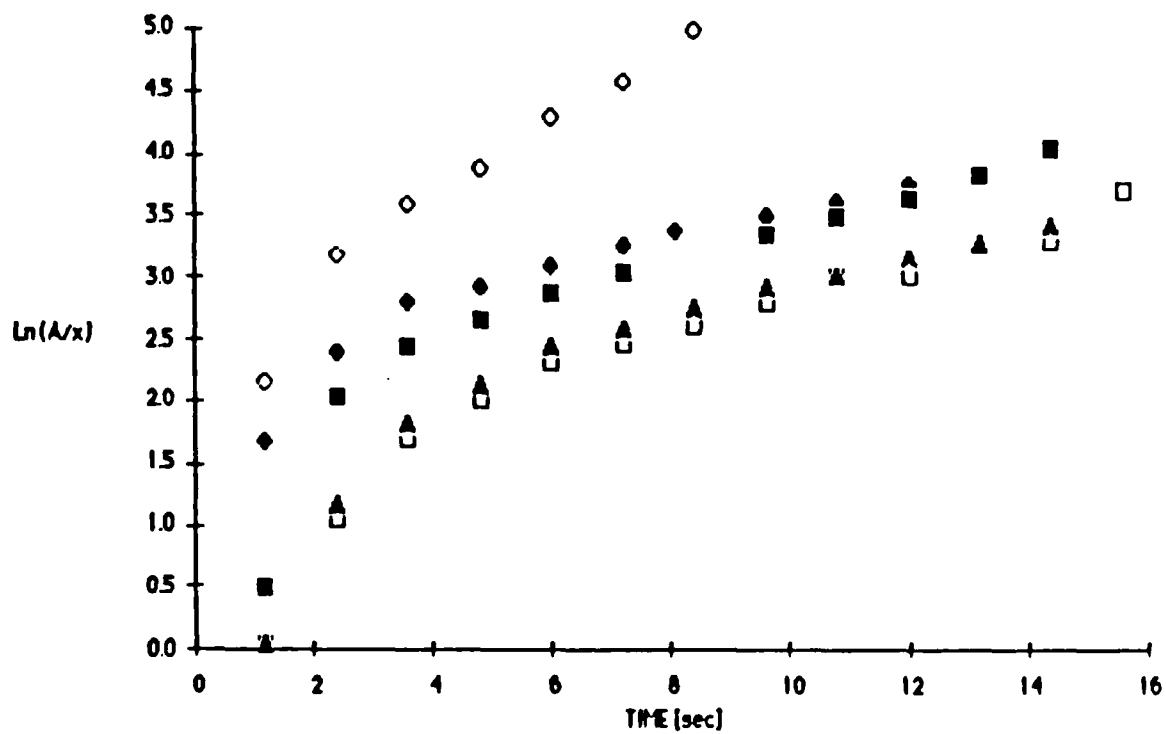
Fig. 4

Fig. 5

Fig. 6

Fig. 7

100mV

air | nitrogen

6min

TIME

0
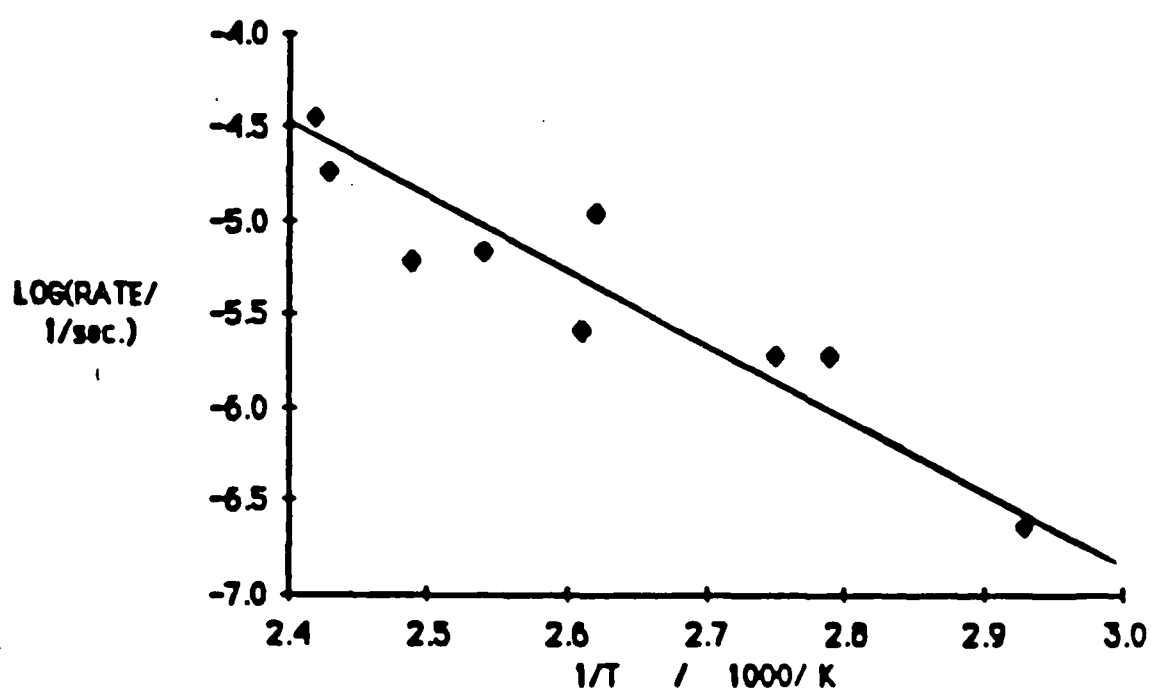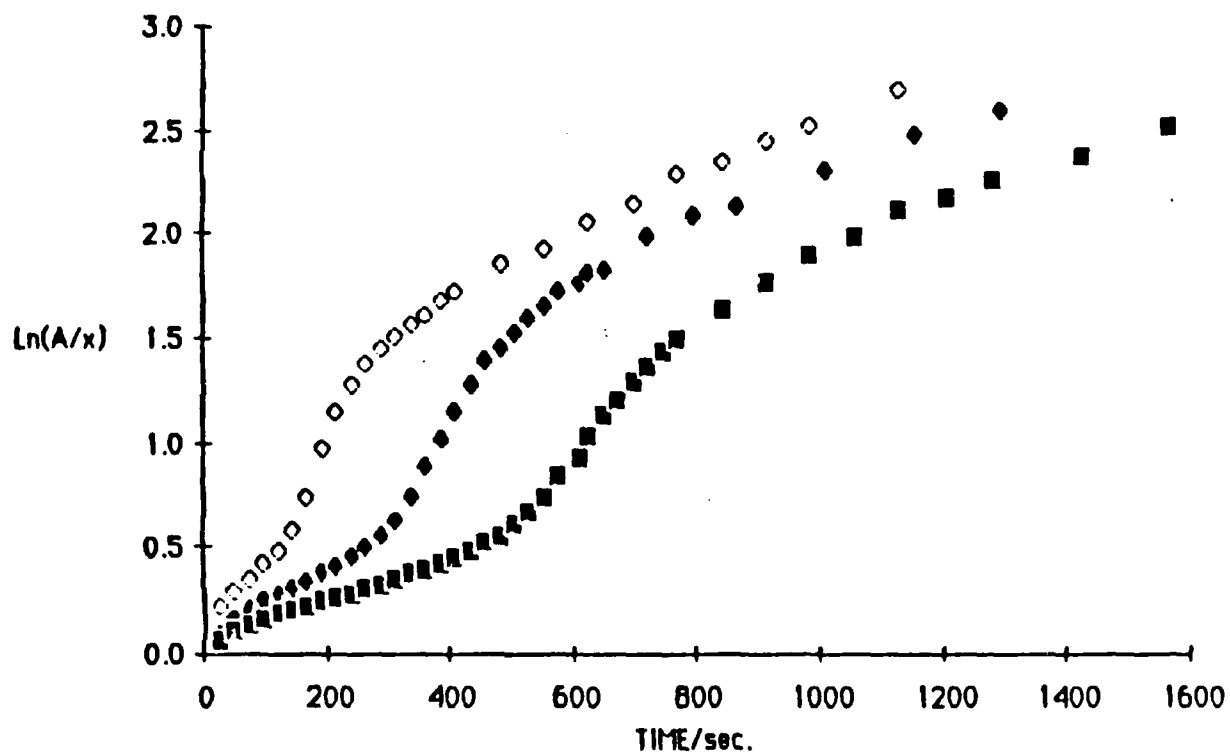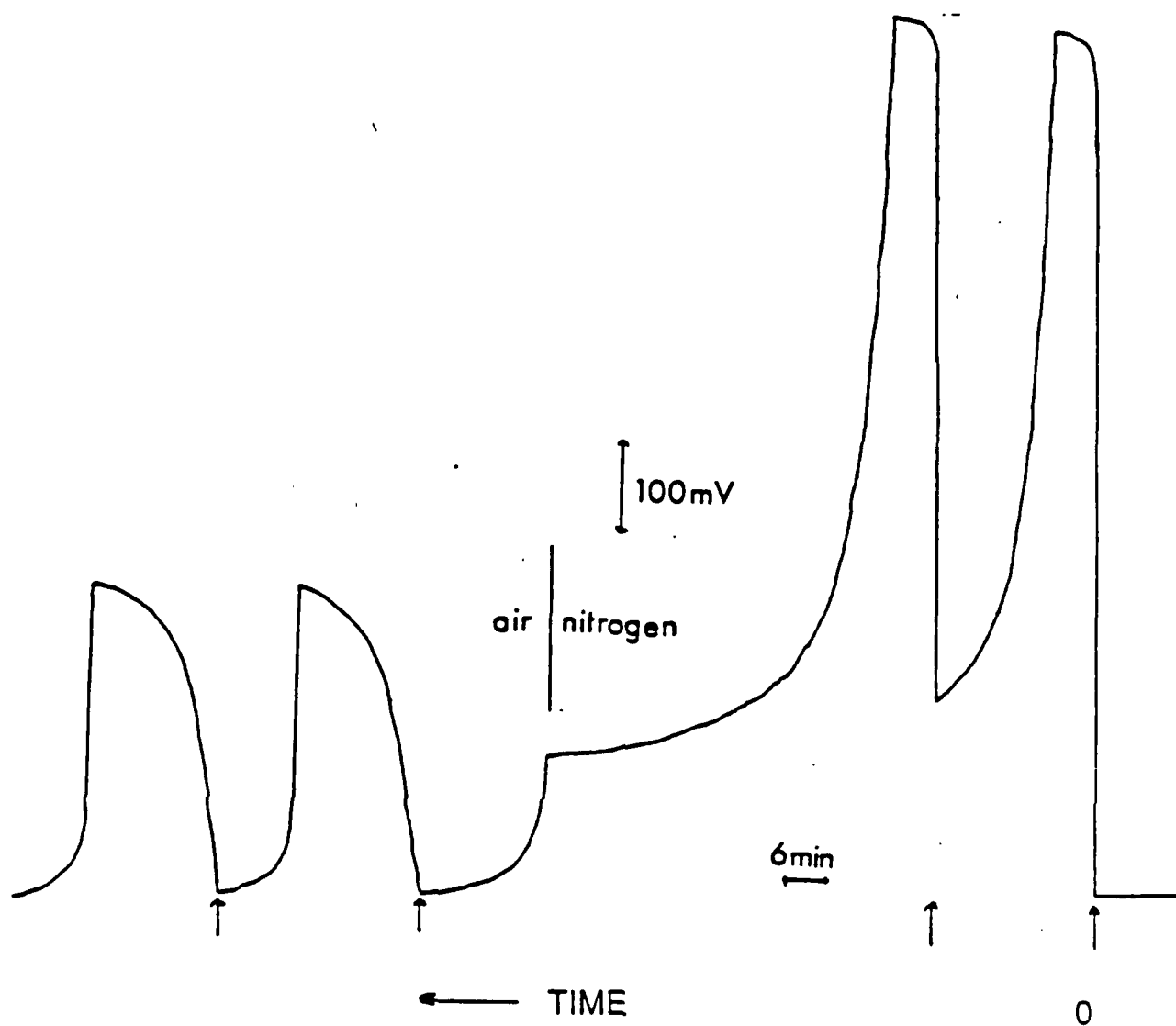
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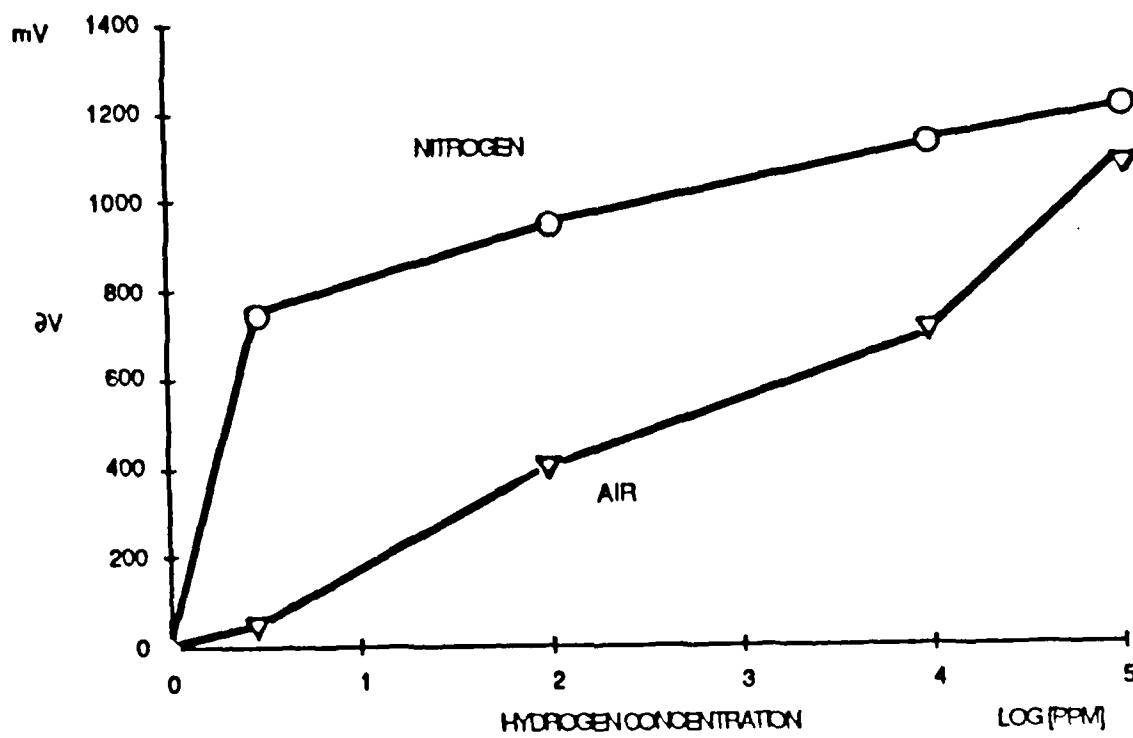
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